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Introduction

This final report consists of four manuscripts submitted for publication which describe the positive results obtained during this research. This work was carried out during October 1, 1958 through May 31, 1961. Experimental work was performed by Dr. K. A. Brändle, Mr. T. Wada and Dr. T. O. Read (Research Associates) and Mr. S.O. Grim (graduate student). Dr. George E. Murray, QMREC, QM Research and Development Center, Natick, Massachusetts, was Project Officer.

The manuscripts in this report include:

"Studies in Phosphinemethylene Chemistry. IV. The Reaction of Triphenylphosphinemethylene and Triphenylphosphinevinylmethylene with Phenylbromophosphines", D. Seyferth and K. A. Brändle, J. Am. Chem. Soc., 83, 2055 (1961).

"Studies in Phosphinemethylene Chemistry. III. Triphenylphosphinechloromethylene", D. Seyferth, S. O. Grim and T. O. Read, J. Am. Chem. Soc., 83, 1617 (1961).

"Vinyl Compounds of Metals. XI. Reaction of Nucleophilic Reagents with Triethylperfluorovinylsilane", D. Seyferth and T. Wada (to be submitted to Inorg. Chemistry).

"Vinyl Compounds of Metals. XII. Some Addition Reactions of Triethylperfluorovinylsilane. The F^{19} Nuclear Resonance Spectra of Triethylperfluorovinylsilane, Triethylperfluorovinylgermane and Triethylperfluorovinyltin", D. Seyferth, T. Wada and G. E. Maciel (to be submitted).

Not included are two preliminary communications describing some of this work:

"The Reaction of Organolithium Reagents with Perfluorovinyl Derivatives of Tin and Silicon", D. Seyferth, T. Wada and G. Raab, Tetrahedron Letters, 1960, No. 22, 20.

"A New Preparation of Triphenylphosphinemethylenes by the Reaction of Carbenes with Triphenylphosphine", D. Seyferth, S. O. Grim and T. O. Read, J. Am. Chem. Soc., 82, 1510 (1960).

since the full papers in this report give all the details.

[Contribution from the Department of Chemistry of the

Massachusetts Institute of Technology]

Studies in Phosphinemethylene Chemistry. III. Triphenylphosphinechloro-

methylene.[1]

By Dietmar Seyferth, Samuel O. Grim and Terence O. Read

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(1)   This work was summarized in part in a preliminary communication:
      D. Seyferth, S.O. Grim and T.O. Read, This Journal, 82, 1510 (1960).
      For part II, see This Journal, 83, 0000 (1961).

Triphenylphosphinechloromethylene has been prepared by the reaction

of triphenylphosphine and chlorocarbene and by the action of phenyllithium

on chloromethyltriphenylphosphonium bromide. Examples of its use in the

Wittig reaction are given; this represents a new general synthesis of vinylic

chlorides of the type RCH:CHCl and R_2C:CHCl.

The electrophilic nature[2] of halocarbenes is believed to be due

(2) (a) W. von E. Doering and A. K. Hoffmann, This Journal, 76, 6162 (1954);
     (b) J. Hine and A. M. Dowell, ibid., 76, 2688 (1954); (c) P. S. Skell
     and A. Y. Garner, ibid., 78, 5430 (1956); W. von E. Doering and W. A.
     Henderson, ibid., 80, 5274 (1958).

to their electronic structure where carbon is in the singlet ground state,

in which an electron pair fills a carbon sp^2 orbital not used in bonding,

leaving the p_z orbital vacant. If this description of carbenes is accepted,

then triphenylphosphinemethylenes, $(C_6H_5)_3P\overset{+}{-}\overset{..}{C}X_2 \longleftrightarrow (C_6H_5)_3P=CX_2$, can be

regarded as donor-acceptor complexes formed between the nucleophile triphenyl-

phosphine and the electrophilic carbene. This suggested that the direct reac-

tion between triphenylphosphine and carbenes might provide a new synthesis of

the useful triphenylphosphinemethylene reagents. The heretofore unknown tri-

phenylphosphinehalomethylenes would be of interest, since their study would

allow an assessment of the inductive effect of electronegative substituents

on the methylene carbon as a possible contributing factor to the stability

of phosphinemethylenes. They would also be of synthetic importance in organic

chemistry, especially if they would undergo the Wittig reaction[3], since this

(3) G. Wittig and U. Schöllkopf, Chem. Ber., 87, 1318 (1954); see also
     U. Schöllkopf, Angew. Chem., 71, 260 (1959).

would result in a new general synthesis of vinyl and vinylidene halides.

  We report here the trapping of chlorocarbene with triphenylphos-

phine and the use of the resulting triphenylphosphinechloromethylene in the

Wittig reaction.

When chlorocarbene was generated by adding ethereal butyllithium to methylene chloride in ether at -30° [4] in the presence of triphenylphos-

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(4) G. L. Closs and L. E. Closs, This Journal, 81, 4996 (1959).

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phine, the deep yellow-orange color characteristic of phosphinemethylene reagents developed. This mixture (a moderate amount of yellow-brown solid also was always present) reacted with ketones and aldehydes to produce the expected 1-chloroölefins in yields averaging ca. 30%. In this manner aceto-phenone was converted to 1-chloro-2-phenyl-1-propene; diethyl ketone to 1-chloro-2-ethyl-1-butene; 4-methyl-2-pentanone to 1-chloro-2,4-dimethyl-1-pentene; cyclohexanone to chloromethylenecyclohexane; and

$$(C_6H_5)_3P + :CHCl \longrightarrow (C_6H_5)_3P=CHCl \xrightarrow{R_2C=O} R_2C=CHCl + (C_6H_5)_3PO$$
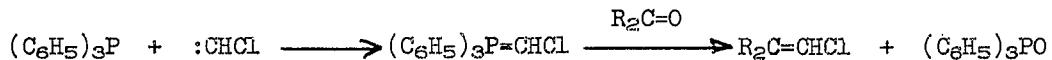
benzaldehyde to β-chlorostyrene. In the acetophenone reaction the two geo-metric isomers of 1-chloro-2-phenyl-1-propene were, as detected by gas chroma-tography, formed in about equal amounts. In the reactions with benzaldehyde and 4-methyl-2-pentanone the two possible isomers of each chloroölefin may have been present, but they were not resolved in the gas chromatographic analysis of the reaction products.

In an attempt to determine the cause of the low overall yields of chloroölefins, each of the two steps of this synthesis was investigated separately. The known reaction of triphenylphosphinemethylenes with hydro-gen halides, which produces crystalline phosphonium salts in apparently

quantitative yield, was used to determine the yield of triphenylphosphine-chloromethylene formed in the trapping reaction. Hydrogen bromide was bubbled into the triphenylphosphinemethylene solutions formed under various reaction conditions to convert the phosphinemethylene into ether-insoluble chloromethyltriphenylphosphonium bromide. The unreacted triphenylphosphine present in the reaction mixture also reacted with hydrogen bromide to form ether-insoluble triphenylphosphonium bromide, $[(C_6H_5)_3PH]Br$. Separation of these two phosphonium salts was made possible by the instability of the latter in water. An independent experiment showed that when triphenylphosphonium bromide was placed in water, it decomposed to water-insoluble triphenylphosphine and hydrobromic acid. Thus solution of the phosphonium salt mixture in water caused precipitation of triphenylphosphine and left an acidic solution containing the chloromethyltriphenylphosphonium ion. Filtration was followed by addition of aqueous sodium tetraphenylborate to the filtrate, which resulted in quantitative precipitation of chloromethyltriphenylphosphonium tetraphenylborate. The yield of this derivative allowed calculation of the triphenylphosphinechloromethylene yield. The accuracy of this method was shown by analyzing four mixtures of pure chloromethyltriphenylphosphonium bromide and pure triphenylphosphonium bromide of known composition. The chlorocarbene capture reaction was repeated many times, using different ratios of reactants, but the yield did not seem to change in any sensible manner, varying from 44 to 68%.

Pure chloromethyltriphenylphosphonium bromide was obtained by re-crystallization of the product of the hydrogen bromide-triphenylphosphine-

chloromethylene reaction. This salt, suspended in ether, reacted with phenyllithium to form an orange solution of triphenylphosphinemethylene; a moderate amount of yellow solid was present as well. The reaction of this mixture with acetophenone and benzaldehyde afforded 1-chloro-2-phenyl-1-propene (91%) and β-chlorostyrene (76%) respectively. Other conversions are described in the experimental section.

Thus when triphenylphosphinechloromethylene was prepared by the dehydrohalogenation of chloromethyltriphenylphosphonium bromide, much better yields were obtained in the subsequent Wittig reactions than when the phosphinemethylene reagent was prepared by trapping chlorocarbene with triphenylphosphine. This probably is due to the formation of triphenylphosphinechloromethylene in much better yield in the former method and also to the absence of excess triphenylphosphine, which appears to make isolation of the chloroölefins more difficult when the phosphinemethylene reagent was prepared by the latter method. For preparation of 1-chloroölefins by the Wittig procedure, it is recommended that the chloromethyltriphenylphosphonium bromide-phenyllithium reaction be used to generate triphenylphosphinechloromethylene, and that the required chloromethylphosphonium salt be prepared by the procedure reported recently by Hoffmann[5].

(5) H. Hoffmann, _Angew Chem._, _72_, 77 (1960).

After a report of the present work had been submitted as a preliminary communication[1], a paper by Speziale, Marco and Ratts[6] reported that

(6) A. J. Speziale, G. J. Marco and K. W. Ratts, _This Journal_, _82_, 1260 (1960).

dichlorocarbene could be captured with triphenylphosphine and that the resulting triphenylphosphinedichloromethylene could be used in the Wittig reaction. Wittig and Schlosser[7] reported the chlorocarbene-triphenylphos-

(7) G. Wittig and M. Schlosser, Angew. Chem., 72, 324 (1960).

phine reaction and the use of triphenylphosphinechloromethylene in chloro-ölefin synthesis shortly after our initial report, and further work by Wittig and Franzen[8] showed that CH_2, generated in the decomposition of tri-

(8) V. Franzen and G. Wittig, ibid., 72, 417 (1960).

methylammoniummethylide, could be trapped with triphenylphosphine.

The early work of Staudinger and Meyer[9] is of interest in this

(9) H. Staudinger and J. Meyer, Helv. Chim. Acta, 2, 619 (1919).

connection. Their synthesis of the first triphenylphosphinealkylidene, $(C_6H_5)_3P=C(C_6H_5)_2$, was effected by thermal decomposition of the phosphazine, $(C_6H_5)_3P=N-N=C(C_6H_5)_2$. It is possible (but not proven) that this reaction involves decomposition to triphenylphosphine, nitrogen and $(C_6H_5)_2C$, followed by combination of triphenylphosphine and diphenylmethylene. Evidence has been presented[10] that $(C_6H_5)_2C$ is a diradical species in which the methylene

(10) R. M. Etter, H, S. Skovronek and P. S. Skell, This Journal, 81, 1008 (1959).

carbon atom is in a triplet state rather than in a singlet state. Reactions of triphenylphosphine with radical reagents have been reported[11,12], and

(11) F. Ramirez and N. McKelvie, ibid., 79, 5829 (1957).

(12) L. Horner and H. Hoffmann, Chem. Ber., 91, 45; 50 (1958).

so the formation of a phosphinemethylene in a reaction of triphenylphosphine with a diradical does not seem impossible. This presents the interesting possibility that triphenylphosphinemethylenes could result from reactions of triphenylphosphine with divalent carbon species in the triplet or the singlet ground state.

EXPERIMENTAL[13]

(13) Analyses were performed by Dr. S. M. Nagy (M. I. T.) and by the
      Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. Melting
      points were determined using a Mel-Temp melting point apparatus.
      All reactions involving the preparation or use of organolithium
      reagents were carried out under an atmosphere of prepurified
      nitrogen. Starting materials either were purchased, and if nec-
      essary, subjected to further purification, or were prepared by
      methods described in the literature.

1) Preparation of Triphenylphosphinechloromethylene from Triphenylphosphine and Chlorocarbene, and Its Reaction with Hydrogen Bromide. - Triphenylphosphine (30 g., 0.115 mole) was placed in a 500 ml., three-necked round bottom flask equipped with an additional funnel, a mechanical stirrer and an inlet tube which protruded half-way into the flask. This tube was connected to a

three-way stopcock which led to the nitrogen atmosphere system and to a
cylinder of anhydrous hydrogen bromide (Matheson Company). Anhydrous
ether (200 ml.) and 11 g. (0.13 mole) of methylene chloride, freshly dis-
tilled from phosphorus pentoxide, were added. The flask was immersed in
a Dry Ice-acetone bath maintained at -40° to -30°, and 40 ml. of 2.48M
(0.10 mole) of n-butyllithium solution was added slowly with vigorous
stirring. The solution became yellow at first and the color deepened to
orange as the addition progressed. After the addition had been completed,
the addition funnel was replaced by a connecting tube which was attached
to a mercury overpressure valve. The cooling bath was removed. As hydro-
gen bromide was bubbled into the flask, the orange color was discharged
immediately with formation of copious quantities of white precipitate. The
resulting mixture was filtered through a sintered glass filter funnel; the
solids were washed with benzene and petroleum ether and dried in vacuum at
60° for 12 hrs. The dried product weighed 33.6 g. A sample of this solid
(0.4983 g.) was placed in 40 ml. of water; the solid was broken up with a
stirring rod and the mixture stirred for 10 min. in order to insure solution
of the chloromethyltriphenylphosphonium bromide and complete decomposition
of triphenylphosphonium bromide. The mixture was filtered and the filtrate
collected in a 400 ml. beaker. The beaker in which the solution had been
prepared and filter paper, as well as the solid, were washed carefully with
successive small portions of water, the washings being added to the filtrate.
A solution of ca. 0.5 g. of sodium tetraphenylborate in 20 ml. of water was
then added dropwise to the filtrate. The mixture was stirred during the

addition to effect rapid coagulation of the resulting precipitate. The in-soluble chloromethyltriphenylphosphonium tetraphenylborate was collected by filtration using a tared Gooch-type filter funnel with a sintered glass fil-ter. The residue was washed with water and dried in vacuum over phosphorus pentoxide. The dry tetraphenylborate weighed 0.6163 g., which corresponded to a product composition of 76.7% chloromethyltriphenylphosphonium bromide and an overall yield (based on butyllithium) of 65.7%.

The reaction was repeated several times with varying ratios of reagents. The results are listed in Table I.

TABLE I

Triphenylphosphinechloromethylene via the Reaction of Triphenylphosphine with Chlorocarbene

$(C_6H_5)_3P$, moles	n-BuLi, moles	CH_2Cl_2, moles	Yield, %
0.115	0.10*	0.13	66 (a)
.115	.20	.10*	53
.085*	.14	.14	56
.60	.60	.65	44 (b)
.229	.076* (c)	.10	54

* Limited reagent; yields based on this figure.

(a) recrystallized yield: 46%
(b) recrystallized yield: 32%
(c) phenyllithium used instead of butyllithium

Determination of the Composition of Mixtures of Chloromethyltriphenylphos-phonium Bromide and Triphenylphosphonium Bromide. - Triphenylphosphonium bromide (0.0469 g.) and chloromethyltriphenylphosphonium bromide (0.1750 g.) were placed in 20 ml. of water, and operations for the precipitation, filtra-

tion, drying and weighing of chloromethyltriphenylphosphonium tetraphenyl-
borate were repeated as described above. This procedure was tested for
several product compostions. The results are given in Table II.

TABLE II

Analysis of Mixtures of Triphenylphosphonium Bromide and Chloromethyltri-
phenylphosphonium Bromide.

[ϕPH]Br (g.)	[ϕ_3PCH$_2$Cl]Br (g.)	[ϕPCH$_2$Cl]Br (%)	[ϕ_3PCH$_2$Cl][Bϕ_4](g.)	
			found	calcd.
0.0469	0.1750	79	0.2825	0.2819
.1025	.1985	67	.3152	.3198
.0380	.2281	86	.3675	.3675
0	.2782	100	.4470	.4482

Recrystallization of Chloromethyltriphenylphosphonium Bromide and Prepara-
tion of Derivatives. - Pure chloromethyltriphenylphosphonium bromide from
the triphenylphosphinemethylene-hydrogen bromide reaction was isolated as
follows: 2.0 g. of the reaction product was dissolved in 8 ml. of iso-
propanol and filtered; to the filtrate was added 300 ml. of ether. The
resulting precipitate was filtered, washed with ether and dried. The
slightly yellow solid, m.p. 195-208°, weighed 0.92 g. Another recrystalliza-
tion resulted in pure material, white solid of m.p. 209-11°.

Anal. Calcd. for C$_{19}$H$_{17}$BrClP: C, 58.26; H, 4.38; Cl, 9.05; Br, 20.40.

Found: C, 58.47; H, 4.31; Cl, 8.56; Br, 20.31.

Picrate. - A sample of chloromethyltriphenylphosphonium bromide, 0.5 g., was
dissolved in 30 ml. of water and added to an excess of picric acid dissolved
in 20 ml. of 1:1 methanol-water mixture. The solution was heated and more

methanol was added to dissolve the precipitate that had formed. The solution was filtered, and on cooling, the filtrate yielded yellow crystals. These were recrystallized from methanol; m.p. 192-94°.

Anal. Calcd. for $C_{25}H_{19}ClN_3O_7P$: C, 55.61; H, 3.55; Cl, 6.56.

Found: C, 55.60; H, 3.76; C, 6.32.

Tetraphenylborate. - This derivative was prepared as described above and was recrystallized from methanol-ether to give pure material, m.p. 189-92°.

Anal. Calcd. for $C_{43}H_{37}ClPB$: C, 81.84; H, 5.91; Cl, 5.62.

Found: C, 82.03; H, 6.17; Cl, 5.37.

2) Preparation of Triphenylphosphinechloromethylene from Triphenylphosphine and Chlorocarbene, and Its Reaction with Ketones. - Triphenylphosphine (30 g., 0.115 mole) was placed in a 500 ml., three-necked flask equipped with an addition funnel, stirrer and condenser topped with a nitrogen inlet tube. Anhydrous ether (230 ml.) and methylene chloride (11 g., 0.13 mole) were added. The flask was cooled to -40° to -30°. The mixture was stirred rapidly while 77 ml. of 1.3M (0.1 mole) n-butyllithium solution was added slowly over a period of one hr. After the addition had been completed, the solution was orange, and a considerable amount of yellow solid was present. When acetophenone (12 g., 0.1 mole), recently distilled and stored over Linde 5A Molecular Sieves, was added, the orange solution immediately turned light yellow and more solid was formed. This mixture was heated at reflux for 10 hrs.; subsequently the ether was removed by distillation. The residue dissolved completely in 120 ml. of tetrahydrofuran, and this solution was heated at reflux for six hrs. The tetrahydrofuran solution was shaken

with 100 ml. of water, and the layers were separated. This operation was repeated. The aqueous extracts were then washed with pentane and the washings added to the organic layer. After removal of the solvents by distillation, the head temperature rose rapidly. The distillate, 7.52 g., was collected from 84°/15 mm. to 120°/15 mm.; it was analyzed using vapor phase chromatography[14] and was found to be composed of 1-chloro-2-phenyl-1-pro-

(14) Gas chromatography columns[15] were 8 mm. Pyrex tubes of 190 cm. length containing 30% be weight of Dow Corning Silicone Oil No. 550 on 48-80 mesh firebrick support. The columns were operated at the temperatures of 120-190°, depending on the b.p. of the compounds chromatographed. Helium at 15 p.s.i. was the carrier gas, and thermistors were employed for detecting sample peaks. Collection of samples was made in a cooled small trap fitted with "no-air" stoppers and a Drierite drying tube. At the moment the sample peak was detected by the automatic recorder, the trap was placed on the hypodermic needle attached to the column exit. Percent composition analyses were approximated by assuming that the area under the curve is proportional to the mole percent of the constituents.[16]

(15) A. C. Cope and P. E. Peterson, This Journal, 81, 1647 (1959).

(16) A. I. M. Keulemans, "Gas Chromatography", Reinhold, New York, 1957, pp. 31-2.

pene (both isomers) (56%) acetophenone (40%) and impurities (4%). These results established that the chloroölefin had been obtained in 28% yield (based on butyllithium).

A sample of distillate, 7.9 g., from another reaction similar to the one described above was dissolved in 10 ml. of pentane and chromatographed using 120 g. of Merck reagent aluminum oxide in a water-jacketed column. The first 500 ml. eluted with pentane was freed of solvent by distillation. The

residue, 4.9 g., contained some ketone (positive 2,4-dinitrophenylhydrazine test), and for this reason was chromatographed again. Distillation of the pentane from the first five 100 ml. portions of eluate left as residue 0.37 g., 1.97 g., 0.41 g., 0.11 g., and 0.0 g. of liquid respectively. Vapor phase chromatographs of these fractions showed that the geometric isomers expected for 1-chloro-2-phenyl-1-propene were present, with the lower boiling isomer increase in relative amounts in the successive fractions. No ketone or other impurities were detected by vapor phase chromatography. A sample of the third fraction was subjected to a short path distillation; the distillate, $n_D^{25}1.5539$, was a nearly 1:1 mixture of the isomers.

Anal. Calcd. for C_9H_9Cl: C, 70.82; H, 5.94. Found: C, 70.81; H, 5.95.

Infrared spectrum (pure liquid): 3080(m), 2980(m), 1610(m), 1602(m), 1572(w), 1495(s), 1436(s), 1370(m), 1322(m), 1240(w), 1204(w), 1071(m), 1029(s), 1010(s), 985(m), 911(m), 831(s), 790(s), 748(s), 690(s) cm^{-1}.

A number of runs were carried out in which reagent ratios were varied. The best yield (46%) resulted when the reaction was effected with 0.11 mole of triphenylphosphine, 0.1 mole of methylene chloride, 0.2 mole of butyllithium and 0.2 mole of acetophenone. It is likely that careful study of conditions may result in better yields, but this aspect of the problem will not be investigated further.

Similar reactions were carried out in which triphenylphosphine-chloromethylene prepared from the triphenylphosphine-chlorocarbene reaction was treated with other ketones. The following chloroolefins were prepared. 1-Chloro-2,4-dimethyl-1-pentane (from 4-methyl-2-pentanone), 27% isolated

yield, n_D^{25} 1.4339.

Anal. Calcd. for $C_7H_{13}Cl$: C, 63.39; H, 9.88. Found: C, 63.44; H, 9.89.

1-Chloro-2-ethyl-1-butene (from diethyl ketone), 20% yield, n_D^{25} 1.4369.

Anal. Calcd. for $C_6H_{11}Cl$: C, 60.74; H, 9.30. Found: C, 60.78; H, 9.40.

Chloromethylenecyclohexane (from cyclohexanone), 30% yield n_D^{25} 1.4829.

Anal. Calcd. for $C_7H_{11}Cl$: C, 64.36; H, 8.49. Found: C, 64.24; H. 8.48.

3) Preparation of Triphenylphosphinechloromethylene from Chloromethyltri-phenylphosphonium Bromide and Phenyllithium, and Its Reaction with Ketones. -

A sample of chloromethyltriphenylphosphonium bromide (6.23 g., 0.0159 mole) was placed in a 300 ml., three-necked flask equipped in the manner described in the previous experiment. After the air in the system had been displaced with nitrogen, 80 ml. of anhydrous ether was added and 17 ml. of 0.93M phenyl-lithium solution (0.0158 mole) was added rapidly. The mixture (some solid was always present) was orange after it had been stirred for 30 min. at room temperature. Acetophenone (4.5 g., 0.038 mole) was added, and the mixture was heated for 23 hrs. without stirring. During the last 10 hrs. the ether solvent was distilled off slowly, and the residue was heated at higher tem-perature. The mixture was distilled without filtering. The distillate, 3.54 g., was collected from 80-125°/15 mm. The yield of the two isomers of 1-chloro-2-phenyl-1-propene, present in 56:44 molar ratio, was 91% (vapor phase chromatography).

Other conversions carried out in a similar manner were: cyclo-hexanone to chloromethylenecyclohexane (80%); 4-methylcyclohexanone to chloromethylene-4-methylcyclohexane[17] (51%); diethyl ketone to 1-chloro-2-

(17) Not completely pure. n_D^{25} 1.4800. Anal. Calcd. for $C_8H_{13}Cl$: C, 66.43; H, 9.06. Found: C, 65.42; H, 8.92.

ethyl-1-propene (66%); 4-methyl-2-pentanone to 1-chloro-2,4-dimethyl-1-pentane (60%); benzaldehyde to β-chlorostyrene[18] (76%).

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(18) n_D^{25} 1.5728. Anal. Calcd. for C_8H_7Cl: C, 69.33; H, 5.09. Found: C, 69.50; H, 5.25.

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4) Reaction of Triphenylphosphine with Hydrogen Bromide. - Triphenylphosphine (3.06 g., 0.0116 mole) was dissolved in 60 ml. of ether, and hydrogen bromide was bubbled into the solution. The white solid which resulted was filtered, washed with ether and dried. A 96% yield (3.85 g.) was obtained. The product was very soluble in methylene chloride and was recrystallized from methylene chloride by adding ether. The resulting triphenylphosphonium bromide decomposed between 170-198°.

Anal. Calcd. for $C_{18}H_{16}BrP$: C, 62.99; H, 4.70. Found: C, 63.20; H, 4.69.

In addition, 0.2228 g. of the solid was placed in 30 ml. of water and stirred for a short time. The triphenylphosphine was filtered off and washed. The filtrate and washings required 5.54 ml. of 0.1164N NaOH for titration of the HBr formed in the decomposition of triphenylphosphonium bromide. Calcd. for $C_{18}H_{16}BrP$: HBr: 23.58; Found: 23.42.

The tetraphenylborate, $[\phi_3PH][B\phi_4]$, could be prepared by mixing concentrated solutions of triphenylphosphonium bromide and sodium tetraphenylborate in methanol. The resulting white crystals decomposed beginning ca. 170° to a brown melt at 200°.

Anal. Calcd. for $C_{42}H_{36}PB$: C, 86.59; H, 6.23. Found: C, 86.89; H, 6.69

Cambridge 39, Massachusetts

[Contribution from the Department of Chemistry of the

Massachusetts Institute of Technology,

Cambridge, Massachusetts.]

Studies in Phosphinemethylene Chemistry. IV. The Reaction of Triphenyl-

phosphinemethylene and Triphenylphosphinevinylmethylene with Phenylbromo

phosphines.[1]

By Dietmar Seyferth and Karl A. Brändle

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(1) This work was summarized in part at the XVII International Congress of
Pure and Applied Chemistry, München, August 30 - September 6, 1959; cf.
Angew..Chem., 72, 65 (1960). For Part III, see D. Seyferth, S. O. Grim
and T. O. Read, J. Am. Chem. Soc., 83, 0000 (1961).

The reaction of triphenylphosphinemethylene with diphenylbromophos-

phine produces diphenylphosphinomethyltriphenylphosphonium bromide; similar

products are produced in the reaction of triphenylphosphinemethylene with

phenyldibromophosphine and dimethylbromostibine and of triphenylphosphine-

vinylmethylene with diphenylbromophosphine. The bromination of $[(C_6H_5)_3PCH-$

$(CH=CH_2)P(C_6H_5)_2]Br$ is of interest, since the initial step apparently is

the formation of the insoluble tribromide salt of this cation; the latter

then is the active brominating agent which gives the product, $[(C_6H_5)_3PCH-$

$(CH=CH_2)P(C_6H_5)_2Br]Br_2$.

It has been established previously that triphenylphosphinemethylene
of metals
reacts with halides of Periodic Groups II and IV to produce organometallic-
substituted phosphonium salts.[2] It was expected therefore that the reaction

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(2) S. O. Grim and D. Seyferth, Chem. and Ind. (London), 849 (1959);
J. Am. Chem. Soc., 83, 0000 (1961).

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of triphenylphosphinealkylidenes with phosphorus halides would proceed in

a similar manner.

This research showed this to be the case. Addition of diphenylbromo-

phosphine to a solution of triphenylphosphinemethylene in ether resulted in

the immediate precipitation of diphenylphosphinomethyltriphenylphosphonium

bromide. Attempts to isolate this product and

$$(C_6H_5)_3P=CH_2 \quad + \quad (C_6H_5)_2PBr \quad \longrightarrow \quad [(C_6H_5)_3PCH_2P(C_6H_5)_2]Br$$
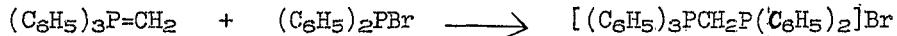
all other phosphonium bromides prepared in this study in the pure crystalline

state were unsuccessful; in all cases oils which could not be crystallized

resulted when recrystallization was attempted. However, the phosphonium

cations formed could be characterized by conversion of the crude bromides

to a suitable insoluble derivative, such as the tetraphenylborate or the

tri- or tetrabromomercurate. In the case of diphenylphosphinomethyltri-

phenylphosphonium bromide, an analytically pure tetraphenylborate could be

prepared. However, the crude bromide reacted with two moles of mercuric

bromide, since two functions capable of complexing mercuric bromide were

present: bromide ion and a trivalent phosphorus atom, and the adduct of

structure I was formed.

$$\left[(C_6H_5)_3PCH_2\overset{\oplus}{P}(C_6H_5)_2 \atop \downarrow \atop HgBr_2 \right] \overset{\ominus}{[HgBr_3]} \qquad I$$
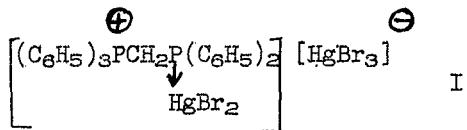
Phenyldibromphosphine reacted with triphenylphosphinemethylene to form a diphosphonium salt, $[(C_6H_5)_3PCH_2P(C_6H_5)CH_2P(C_6H_5)_3]Br_2$, characterized as the bis-tetraphenylborate. Triphenylphosphinevinylmethylene underwent an analogous reaction with diphenylbromophosphine.

These phosphonium salts containing trivalent organophosphorus substituents could be quaternized with methyl bromide to give polyphosphonium salts such as $[(C_6H_5)_3PCH_2P(C_6H_5)(CH_3)CH_2P(C_6H_5)_3]Br_3$ and $[(C_6H_5)_3PCH_2P-(C_6H_5)_2CH_3]Br_2$.

Of particular interest was the bromination of $[(C_6H_5)_3PCH(CH=CH_2)-P(C_6H_5)_2Br$, since this compound contained at first sight two functions capable of reacting with bromine: the olefinic double bond and the trivalent phosphorus atom. The product of the bromination, which was carried out in methanol, was characterized as the complex with mercuric bromide. The anayltical results fit either of two structures: $[(C_6H_5)_3PCH(CH=CH_2)-P(C_6H_5)_2Br_2][HgBr_3]$ or $[(C_6H_5)_3PCH(CH=CH_2)P(C_6H_5)_2Br][HgBr_4]$. In view of the studies of Issleib and Seidel[3] which showed that triorganodibromophosphoranes behaved like phosphonium salts, $[R_3PBr]Br$, in solution, we favor

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(3) K. Issleib and W. Seidel, Z. anorg. u. allgem. Chem., 288, 201 (1956).

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the second structure. The infrared spectrum of the product showed the double bond to be still present. However, the course of the bromination reaction appeared to be more complicated than expected, and the following observations were made. Addition of a small amount of bromine in methanol solution to a solution of the vinyl-containing phosphonium salt immediately produced a yellow flocculent precipitate. The solid dissolved again while

the solution was stirred. Addition of another small portion of bromine solution precipitated more solid which dissolved on stirring. This procedure could be repeated until one equivalent of bromine had been added. Addition of a small excess of bromine produced more precipitate which did not dissolve on stirring. However, addition of more phosphonium salt to this solution caused this precipitate to dissolve. A probable explanation of these observations is that neither the olefinic double bond nor the trivalent phosphorus atom suffer initial attack by the bromine. Instead bromide ion complexes bromine to give tribromide ion, which is known to form insoluble compounds with large inorganic and organic cations. The insoluble $[(C_6H_5)_3PCH(CH=CH_2)P(C_6H_5)_2]Br_3$ then is the active brominating agent, and its bromination of the trivalent phosphorus atom of either its own cation or of another cation in solution shifts the solubility equilibrium until all of the tribromide has dissolved. Finally, when bromination of the trivalent phosphorus present is complete, addition of bromine in excess precipitates a tribromide which does not dissolve again, since bromine transfer to phosphorus can no longer take place. The equations below summarize this reaction sequence.

$$[\phi_3\overset{\oplus}{P}CH(CH=CH_2)P\phi_2] \;+\; \overset{\ominus}{Br} \;+\; Br_2 \;\longrightarrow\; [\phi_3PCH(CH=CH_2)P\phi_2]Br_3 \;_{(s)}$$

$$[\phi_3PCH(CH=CH_2)P\phi_2]Br_3 \;+\; [\phi_3\overset{\oplus}{P}CH(CH=CH_2)P\phi_2] \;\longrightarrow$$

$$\overset{\ominus}{Br} \;+\; [\phi_3\overset{\oplus}{P}CH(CH=CH_2)P\phi_2] \;+\; [\phi_3\overset{\oplus}{P}CH(CH=CH_2)P\phi_2Br_2]$$

$$[\phi_3\overset{\oplus}{P}CH(CH=CH_2)P\phi_2Br_2] \;\longrightarrow\; [\phi_3\overset{\oplus}{P}CH(CH=CH_2)\overset{\oplus}{P}\phi_2Br] \;+\; \overset{\ominus}{Br}$$

$$[\phi_3\overset{\oplus}{P}CH(CH=CH_2)\overset{\oplus}{P}\phi_2Br] \;+\; HgBr_2 \;\longrightarrow\; [\phi_3PCH(CH=CH_2)P\phi_2Br][HgBr_4] \;_{(s)}$$
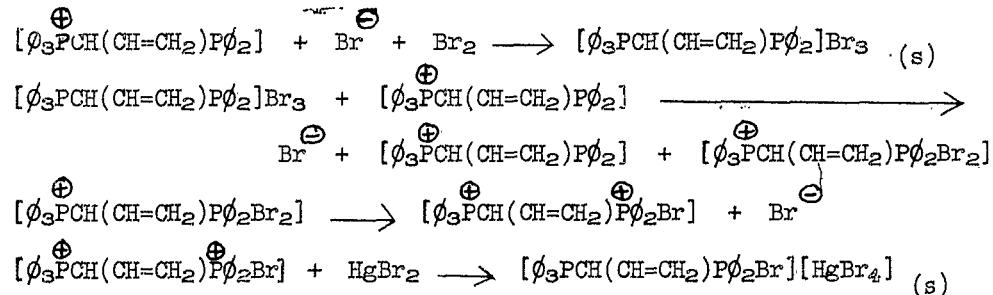
TABLE

Products of the Triphenylphosphinealkylidene - Phenylbromophosphine Reactions

and Their Derivatives

Compound	m.p., °C	Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found
[(C$_6$H$_5$)$_3$PCH$_2$(C$_3$H$_5$)$_2$][B(C$_6$H$_5$)$_4$] a	185.5 - 186	84.61	84.87	6.07	6.20
[(C$_6$H$_5$)$_3$PCH$_2$P(C$_3$H$_5$)$_2$][HgBr$_3$] $\rightarrow$ HgBr$_2$	195 - 196	29.49	29.13	2.16	2.32
[(C$_3$H$_5$)$_3$PCH$_2$P(C$_6$H$_5$)$_2$CH$_3$][B(C$_6$H$_5$)$_4$]$_2$	194°	86.17	85.84	6.33	6.58
[(C$_3$H$_5$)$_3$PCH$_2$P(C$_6$H$_5$)$_2$CH$_3$][HgBr$_3$]$_2$	201	28.32	28.32	2.23	2.39
[(C$_6$H$_5$)$_3$PCH$_2$P(C$_6$H$_5$)CH$_2$P(C$_3$H$_5$)$_3$][B(C$_6$H$_5$)$_4$]$_2$	128 - 130	85.05	84.16	6.13	6.39
[(C$_6$H$_5$)$_3$PCH$_2$P(C$_3$H$_5$)(CH$_3$)CH$_2$P(C$_6$H$_5$)$_3$][B(C$_6$H$_5$)$_4$]$_3$	177 - 179	86.03	85.90	6.30	6.13
[(C$_6$H$_5$)$_3$PCH(CH=CH$_2$)P(C$_6$H$_5$)$_2$][B(C$_6$H$_5$)$_4$]	132 - 133	84.86	83.91	6.12	6.13
[(C$_6$H$_5$)$_3$PCH(CH=CH$_2$)P(C$_6$H$_5$)$_2$CH$_3$][HgBr$_4$]	134 - 135	39.93	39.69	3.15	3.24
[(C$_6$H$_5$)$_3$PCH(CH=CH$_2$)P(C$_6$H$_5$)$_2$CH$_3$][B(C$_6$H$_5$)$_4$]$_2$	137 - 138	86.32	35.62	6.36	6.38
[(C$_6$H$_5$)$_3$PCH(CH=CH$_2$)P(C$_6$H$_5$)$_2$Br][HgBr$_4$]	137 - 138	36.44	36.59	2.69	2.80

a
Hg: Calcd., 31.66; Found, 31.85.

Dimethylbromostibine reacted readily with triphenylphosphinemethylene to give dimethylstibinomethyltriphenylphosphonium bromide, quaternization of which with methyl bromide or methyl iodide resulted in novel mixed phosphonium-stibonium salts, $[\phi_3PCH_2Sb(CH_3)_3]X_2$.

EXPERIMENTAL[4]

(4) Analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. Melting points were determined using a calibrated Fisher-Johns melting point apparatus. All reactions were carried out in an atmosphere of prepurified nitrogen, and all possible precautions were taken to exclude air and moisture from the reaction system before, during and after the reaction.

(1) Reaction of Triphenylphosphinemethylene and Triphenylphosphinevinyl-methylene with Phenylbromophosphines.— The reaction of triphenylphosphine-methylene with diphenylbromophosphine is described to illustrate the procedure used.

To a filtered solution of ca. 0.04 mole of triphenylphosphinemethylene in ether, prepared by the reaction of methyltriphenylphosphonium bromide with phenyllithium[5], was added with vigorous stirring a solution of 10.6 g.

(5) U. Schöllkopf, Angew. Chem., 71, 260 (1959).

(0.04 mole) of diphenylbromophosphine[6] in benzene. The deep yellow phosphine-

(6) Prepared by phenylation of phenyldichlorophosphine (Victor Chemical Works) with diphenylmercury and conversion of the resulting chloride to the bromide by treatment with anhydrous HBr.

methylene solution became lighter in color as the addition progressed, and
a white flocculent solid precipitated. The latter was filtered after the
addition had been completed, washed well with benzene and ether and dried.
The dry solid (19 g.) was a white, moisture-sensitive powder, soluble in
polar solvents such as methanol, ethanol and dimethylformamide (DMF).
Attempted recrystallization or reprecipitation was unsuccessful; either oils
which would not crystallize were obtained, or decomposition resulted.
This general procedure also was used in the reaction of triphenylphosphine-
methylene with phenyldibromophosphine and of triphenylphosphinevinyl-
methylene[5] with diphenylbromophosphine.

(2) Preparation of Derivatives.- Tetraphenylborates.- A solution of
crude diphenylphosphinomethyltriphenylphosphonium bromide in methanol was
added dropwise with stirring to a methanol solution containing an excess of
sodium tetraphenylborate at 0°. A white microcrystalline solid precipitated.
The tetraphenylborate salt thus obtained was dissolved in a small amount of
DMF and reprecipitated by adding the DMF solution to a dilute solution of
sodium tetraphenylborate in methanol. Bromomercurates.- A similar pro-
cedure - the addition of a solution of the crude phosphonium bromide in
methanol to a methanolic solution of mercuric bromide - was used to prepare
the bromomercurate derivatives. Purification of the latter was effected by
adding their DMF solutions to a solution of mercuric bromide in methanol.
Apparently the concentration of the mercuric bromide solutions used in the
precipitation and purification steps is critical in determining whether a
tribromomercurate or a tetrabromomercurate is formed. As can be seen in
Table I, both types of these complex salts resulted in this work. This point

was not investigated further. Quaternization.- A methanolic solution of

crude diphenylphosphinomethyltriphenylphosphonium bromide and a large excess

of methyl bromide were sealed in a pressure bottle and left to stand for

eight days at room temperature. The resulting methanolic solution was

treated with methanolic sodium tetraphenylborate and mercuric bromide, res-

pectively, to prepare the derivatives listed in Table I. The other crude

bromides also were quaternized in this manner.

(3) Dimethylstibinomethyltriphenylphosphonium Bromide and Its Derivatives.-

A slurry of 1.4 g. (0.006 mole) of dimethylbromostibine[7] in ether was added

(7) We are grateful to Dr. Ludwig Maier of Monsanto Research S.A., Zürich, for a sample of this compound.

to a slight excess of triphenylphosphinemethylene in ether. The resulting

heterogeneous reaction mixture was stirred under nitrogen for 40 hours. The

solid was filtered, washed well with ether and dried to give a white powder.

In air this product turned red and decomposed.

One g. of this product was dissolved in 30 ml. of methanol. The

resulting yellow solution was heated at reflux for two hours to give an

orange solution. Addition of methanolic sodium tetraphenylborate to this

solution precipitated methyltriphenylphosphonium tetraphenylborate in 81%

yield, identified by m.p. and mixed m.p.

Three g. of crude dimethylstibinomethyltriphenylphosphonium bromide

and 15 ml. of methyl bromide were stirred under nitrogen for 20 hours in a

flask equipped with a low temperature condenser. The resulting white powder

was washed well with ether and dried (2.9 g.); m.p. 93°.

Anal. Calcd. for $C_{22}H_{26}Br_2PSb$: C, 43.83; H, 4.35. Found: C, 44.10; H, 4.35.

A similar derivative, $[(C_6H_5)_3PCH_2Sb(CH_3)_3]BrI$, was prepared by the reaction of the crude bromide (2.0 g.) with methyl iodide (18 ml.). The resulting light yellow powder (1.7 g.) sintered before it melted at 107 - 110°.

Anal. Calcd. for $C_{22}H_{26}BrIPSb$: C, 40.65; H, 4.03. Found: C, 40.68; H, 4.00.

(Contribution from the Department of Chemistry of the

Massachusetts Institute of Technology,

Cambridge 39, Massachusetts)

Vinyl Derivatives of Metals. XI. Reaction of Nucleophilic Reagents with

Triethylperfluorovinylsilane [1,2]

By Dietmar Seyferth and Tadashi Wada[3]

(1) Preliminary communication: D. Seyferth, T. Wada and G. Raab, _Tetrahedron Letters_, 1960, No. 22, 20.

(2) Part X: D. Seyferth and M. A. Weiner, _J. Am. Chem. Soc._, 83, 0000 (1961).

(3) On leave from the Shin-Etsu Chemical Industry Co., Ltd., Tokyo, Japan.

The reaction of organolithium reagents with triethylperfluorovinylsilane gave _trans_-$Et_3SiCF=CFR$ products (R= n-butyl, phenyl, vinyl, allyl, triphenylsilyl, triphenylgermyl and diphenylphosphinyl), presumably by an addition-elimination sequence. The action of phenyllithium on α,β-difluoro-β-triethylsilylstyrene resulted in formation of triethylphenylsilane and diphenylacetylene. The probable mechanism of this reaction is discussed. Treatment of triethylperfluorovinylsilane with sodium alkoxides and mercaptides also produced addition-elimination products, $Et_3SiCF=CFOR$ and $Et_3SiCF=CFSR$.

Previous studies concerned with the chemical reactivity of vinyl derivatives of Group IV metals have shown that a considerable difference exists between the reactions observed with vinylsilanes and vinylgermanes on one hand and vinyltin and vinyllead compounds on the other[4]. Thus, to cite an example of interest to the present study, triphenylvinylsilane and triphenylvinylgermane react with phenyllithium in the following manner:[5,6]

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(4) For a review see: D. Seyferth, "Vinyl Compounds of Metals" in "Progress in Inorganic Chemistry", Vol. III (F. A. Cotton, editor), Interscience Publishers Inc., New York, N. Y., 1961.

(5) L. F. Cason and H. G. Brooks, $\underline{J.~Am.~Chem.~Soc.}$, $\underline{74}$, 4582 (1952); $\underline{J.}$ $\underline{Org.~Chem.}$, $\underline{19}$, 1278 (1954).

(6) D. Seyferth and M. A. Weiner, $\underline{J.~Am.~Chem.~Soc.}$, $\underline{84}$, 0000 (1962).

$$(C_6H_5)_3MCH=CH_2 \ + \ C_6H_5Li \longrightarrow (C_6H_5)_3\underset{\underset{Li}{|}}{M}CHCH_2C_6H_5 \quad (M=\text{Si and Ge}) \ ,$$
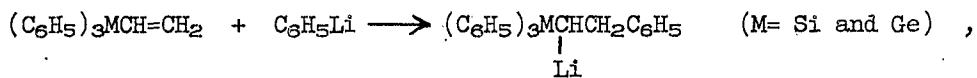
while triphenylvinyltin and triphenylvinyllead undergo an exchange reaction with phenyllithium:[6]

$$(C_6H_5)_3MCH=CH_2 \ + \ C_6H_5Li \longrightarrow (C_6H_5)_4M \ + \ CH_2=CHLi \quad (M=\text{Sn and Pb}) \ .$$
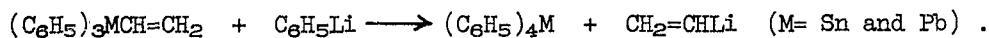
Recent work in these laboratories has shown that perfluorovinyltin compounds also undergo an exchange reaction with organolithium reagents to form the rather unstable perfluorovinyllithium[1]. It therefore was of interest to determine whether an exchange or an addition reaction would be observed on treating perfluorovinylsilanes with organolithium compounds. The results could not be predicted with certainty, since with olefinic silicon compounds both exchange and addition reactions are possible. Which reaction is observed

seems to depend mainly on the nature of the unsaturated group. While the addition reaction is observed with vinylsilanes, the exchange reaction was found to occur with β-styryltriphenylsilane[7] and phenylethynyltriphenylsilane[8].

(7) H. Gilman, T. C. Wu and D. Wittenberg, J. Org. Chem., 25, 596 (1960).

(8) H. Gilman and H. Hartzfeld, J. Am. Chem. Soc., 73, 5878 (1951).

Thus an exchange reaction seemed not unlikely with silicon compounds containing the electronegative perfluorovinyl group.

Triethylperfluorovinylsilane[9] was chosen for this study because of

(9) D. Seyferth, K. A. Brändle and G. Raab, Angew. Chem., 72, 77 (1960).

the relative ease of its preparation. Treatment of this compound with a number of organolithium reagents did not result in an exchange reaction; instead, the products isolated were β-organo-α,β-difluorovinyltriethylsilanes:

$$Et_3SiCF=CF_2 + RLi \xrightarrow{Et_2O} Et_3SiCF=CFR + LiF \quad (R= C_6H_5, CH_2=CH,$$
$$CH_2=CHCH_2, n-C_4H_9)$$
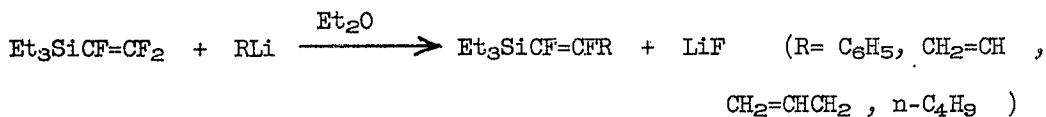
Such products could result either from a direct nucleophilic displacement of a β-fluorine atom by the organolithium reagent or from an addition-elimination sequence:

$$Et_3SiCF=CF_2 + RLi \longrightarrow Et_3SiCFLiCF_2R \longrightarrow Et_3SiCF=CFR + LiF.$$

Similar reactions of simple fluoroolefins, such as tetrafluoroethylene and

chlorotrifluoroethylene, with organolithium reagents have been described previously.[10,11,12,13] Both the addition-elimination path[10,12] and the nucleo-

(10) S. Dixon, J. Org. Chem., 21, 400 (1956).

(11) R. Meier and F. Böhler, Chem. Ber., 90, 2344 (1957).

(12) T. F. McGrath and R. Levine, J. Am. Chem. Soc., 77, 4168 (1955).

(13) G. Bier and H. Fritz, Ger. patent 1,006,852 (1957); C.A., 53, 18862 (1959).

philic substitution mechanism[11] have been suggested for these reactions, but

no conclusive proof for either possibility has been given. For reasons cited[10,12]

we shall accept tentatively the former mechanism and discuss our results in these

terms.

All $Et_3SiCF=CFR$ compounds were stable, distillable liquids. The vinyl-

lithium adduct, 1,2-difluoro-1-triethylsilyl-1,3-butadiene, polymerized on

standing. Similar reactions were observed with triphenylsilyllithium, tri-

phenylgermyllithium and diphenylphosphinyllithium, and the compounds

$Et_3SiCF=CFSi(C_6H_5)_3$, $Et_3SiCF=CFGe(C_6H_5)_3$ (both solids) and $Et_3SiCF=CFP(C_6H_5)_2$,

a liquid, were isolated. Organomagnesium compounds of suitable structure also

were found to undergo such reactions. Thus phenylmagnesium bromide in tetra-

hydrofuran reacted with triethylperfluorovinylsilane to give α,β-difluoro-β-

triethylsilylstyrene in 64% yield. However, ethylmagnesium bromide did not

appear to react with the perfluorovinylsilane in this manner under the same

conditions. Similar observations concerning the relative reactivity of the

phenyl and ethyl Grignard reagents toward 1,1-dichloro-2,2-difluoroethylene

have been described by Tarrant and Warner[14].

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(14) P. Tarrant and D. A. Warner, J. Am. Chem. Soc., 76, 1624 (1954).

The question of the structure of these compounds was examined using F^{19} nuclear resonance spectroscopy. The nuclear resonance spectra of $Et_3SiCF=CFC_6H_5$, $Et_3SiCF=CFSi(C_6H_5)_3$ and $Et_3SiCF=CFGe(C_6H_5)_3$ consisted of a non-equivalence quartet in each case. The F-F spin coupling constants derived were 124, 132 and 144 c.p.s. respectively. In general, F-F spin coupling constants in fluoroolefins are in the range 27-87 c.p.s. for gem-fluorine atoms

( ), 33-58 c.p.s. for cis-fluorine atoms ( ) and 115-124 c.p.s.

for trans-fluorine atoms ( )[15]. It may be noted that attachment of
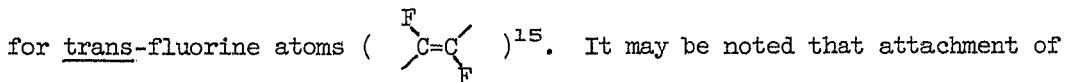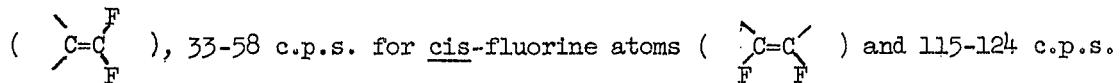
the $CF_2=CF$ group to a silicon atoms does not affect the validity of this generalization, which is based on the F^{19} nuclear resonance spectra of only a few compounds ($CF_2=CFX$, where X is H, Cl, Br, CN and CF_3). The gem, cis and trans F-F spin coupling constants in triethylperfluorovinylsilane are 71, 27 and 116 c.p.s. respectively[16]. The large values of the coupling constants

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(15) H. M. McConnell, C. A. Reilly and A. D. McLean, J. Chem. Phys., 24, 479 (1956).

(16) Unpublished work by Dr. G. E. Maciel in these laboratories.

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observed in the present compounds indicate that the organic group derived from the lithium reagents are on the carbon atom β to the silicon atom, and

that the fluorine atoms are in the <u>trans</u> positions:

$$Et_3Si\diagdown \qquad \diagup F$$
$$C=C$$
$$F \diagup \qquad \diagdown R$$
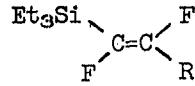
The F^{19} nuclear resonance spectrum of <u>trans</u>-1,2-difluoro-1-triethylsilyl-1-
hexene was that expected for this structure, with an F-F coupling constant
of 126 c.p.s. and further splitting of each line of the quartet into a tri-
plet due to fluorine coupling with the protons of the CH_2 group attached to
the β-carbon atom. A very similar situation obtained in the case of <u>trans</u>-
1,2-difluoro-1-triethylsilyl-1,4-pentadiene.

It is known that tetrafluoroethylene can be converted to tetraphenyl-
ethylene by four successive addition-elimination steps when treated with an
excess of phenyllithium[10]. It therefore was of interest to see if α,β-di-
fluoro-β-triethylsilylstyrene could be converted to more highly phenylated
compounds in this manner. More specifically, the question arose as to which
carbon atom of the olefinic system in <u>trans</u>-$Et_3SiCF=CFC_6H_5$ would be attacked
by phenyllithium. Accordingly, this reaction was carried out with α,β-di-
fluoro-β-triethylsilylstyrene and phenyllithium in 1:1 molar ratio. Neither
$Et_3SiCF=C(C_6H_5)_2$ nor $Et_3SiC(C_6H_5)=CFC_6H_5$ could be isolated; instead the only
products obtained were starting silane, diphenylacetylene and triethylphenyl-
silane. When this reaction was carried out with phenyllithium and the silane
in 2:1 molar ratio, only diphenylacetylene and triethylphenylsilane could be
isolated. These results may be explained as follows: Initial attack of phenyl-
lithium on α,β-difluoro-β-triethylsilylstyrene does indeed give a diphenylated
product. The phenyllithium added subsequently then has the possibility of

reacting either with starting silane or with the diphenylated product. The reaction of the diphenylated product with phenyllithium is one of lithium-silicon exchange, in which triethylphenylsilane and $(C_6H_5)_2CF=CFLi$ or $C_6H_5CF=C(C_6H_5)Li$ are formed. These new lithium reagents would be expected to be unstable under these conditions (note perfluorovinyllithium[1]) and to undergo either α - or β-elimination of lithium fluoride, giving diphenyl-acetylene. The results obtained in the 1:1 reaction indicate that the trans-metalation reaction of phenyllithium with diphenylated product occurs at a much faster rate than the reaction sequence which produces the diphenylated product; starting silane, triethylphenylsilane and diphenylacetylene were isolated in yields of 41%, 50% and 45% (based on the starting silane) respectively. The course of the reaction may be summarized by the following equations.

$$Et_3SiCF=CFC_6H_5 \; + \; C_6H_5Li \longrightarrow LiF \; + \; Et_3SiCF=C(C_6H_5)_2$$

$$(or \; Et_3SiC(C_6H_5)=CFC_6H_5 \;)$$

$$\begin{cases} Et_3SiCF=C(C_6H_5)_2 \; + \; C_6H_5Li \longrightarrow Et_3SiC_6H_5 \; + \; (C_6H_5)_2C=CFLi \\ \qquad or \\ Et_3SiC(C_6H_5)=CFC_6H_5 + C_6H_5Li \longrightarrow Et_3SiC_6H_5 \; + \; C_6H_5CF=C(C_6H_5)Li \end{cases}$$

$$\begin{cases} (C_6H_5)_2C=CFLi \longrightarrow LiF \; + \; C_6H_5C{\equiv}CC_6H_5 \\ \qquad or \\ C_6H_5CF=C(C_6H_5)Li \longrightarrow LiF \; + \; C_6H_5C{\equiv}CC_6H_5 \end{cases}$$
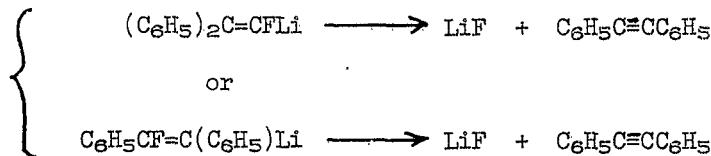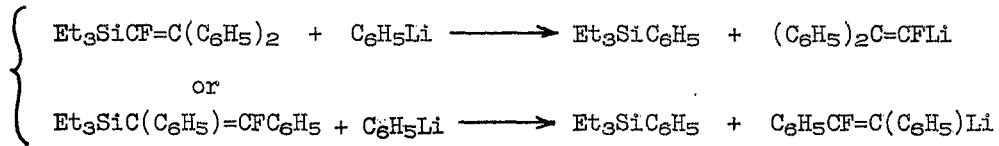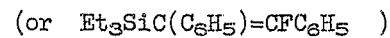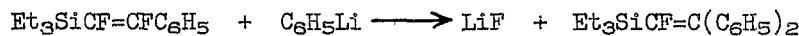
No experimental evidence as to which diphenylated product is formed is available. All experiments carried out under milder conditions with the object of isolating the diphenylated product were unsuccessful. The reported[17] α-elimina-

(17) D. Y. Curtin and E. W. Flynn, J. Am. Chem. Soc., 81, 4714 (1959).

tion of lithium bromide from $(C_6H_5)_2C=CBrLi$ to give diphenylacetylene provides an analogy which favors the β,β-diphenyl structure for our diphenylated intermediate. Work is in progress which may provide further insight into this reaction.

Not only organolithium reagents, but also more conventional nucleophiles will undergo such reactions with triethylperfluorovinylsilane. Treatment of triethylperfluorovinylsilane with ethanolic sodium ethoxide gave, in addition to the cleavage product triethylethoxysilane, the addition-elimination product $Et_3SiCF=CFOC_2H_5$ in 28% yield. Usually saturated products result in such reactions of simple fluoroolefins when carried out in protonic solvents[18]. However, combustion analysis and the infrared and F^{19} nuclear re-

(18) Leading references are given by: D. C. England, L. R. Melby, M. A. Dietrich and R. V. Lindsey, J. Am. Chem. Soc., 82, 5116 (1960), and W. T. Miller, Jr. and A. H. Fainberg, J. Am. Chem. Soc., 79, 4166 (1957).

sonance spectra of the product proved the structure given above. α,β-Difluoro-β-triethylsilylvinyl ethyl ether was obtained in 39% yield when triethylperfluorovinylsilane was added to a slurry of sodium ethoxide in tetrahydrofuran, and the action of sodium trimethylsilylmethoxide in this medium

gave $Et_3SiCF=CFOCH_2SiMe_3$ in 66% yield. Similar reactions with sodium n-propyl-mercaptide and sodium thiophenolate in tetrahydrofuran suspension resulted in $Et_3SiCF=CFSPr$ and $Et_3SiCF=CFSC_6H_5$. Such olefinic products are to be expected in the absence of protonic solvents[19]. The F^{19} nuclear resonance spectra of

(19) R. Meier and F. Bühler, Chem. Ber., 90, 2342 (1957).

both ethers and of the product derived from n-propyl mercaptan indicated that the alkoxy and the propylthio groups were on the carbon atom β to the silicon atom and that the fluorine atoms occupied trans positions. However, the F^{19} spectrum of analytically pure $Et_3SiCF=CFSC_6H_5$ showed the presence of two isomers. In addition to a quartet with an F-F spin coupling constant of 148 c.p.s. indicative of the trans isomer, there was another quartet at lower field with an F-F coupling constant of 20 c.p.s., probably due to the cis isomer. It may be noted in support of this assumption that the F-F coupling constant in cis-1,2-difluoroethylene has been reported to be 18.6 c.p.s.[20]

(20) T. D. Coyle, S. L. Stafford and F. G. A. Stone, J. Chem. Soc., 743 (1961).

The product was determined to contain ca. 74% of the trans isomer and ca. 26% of the cis compound by comparing the areas of the two quartets.

Substitution of a β-fluorine atom in triethylperfluorovinylsilane results in a lowering of the C=C stretching frequency characteristic for that compound (1709 cm^{-1}). The C=C stretching frequencies in $Et_3SiCF=CFOEt$, $Et_3SiCF=CFOCH_2SiMe_3$, $Et_3SiCF=CFCH_2CH=CH_2$ and $Et_3SiCF=CFC_4H_9$ were 1688, 1680,

1672 and 1670 cm^{-1} respectively. Conjugation results in still further lowering as shown by $\nu_{C=C} = 1637$ cm^{-1} in Et$_3$SiCF=CFC$_6$H$_5$. The allyl adduct also showed a band at 1641 cm^{-1} attributable to the C=C stretching frequency of the terminal vinyl group. The spectrum of Et$_3$SiCF=CFCH=CH$_2$ showed weak absorption at 1642 cm^{-1} (shoulder at 1632 cm^{-1}) in addition to strong absorption at 1595 cm^{-1}.

EXPERIMENTAL[21]

Preparation of Triethylperfluorovinylsilane. - To 9.7 g. (0.4 g. atom) of magnesium turnings in a three-necked flask equipped with a stirrer, reflux condenser topped with a nitrogen inlet tube, and a dropping funnel, was added 50 ml. of tetrahydrofuran (THF) and a few drops of 1,2-dibromoethane. The mixture was stirred and cooled to -10° to -15°. Another 100 ml. of THF was added. To this mixture was added, under nitrogen with stirring, a solu-tion of 42 g. (0.28 mole) of triethylchlorosilane and 65 g. (0.4 mole) of bromotrifluoroethylene (Peninsular Chem Research, Inc.) in 200 ml. THF. Stirring was continued for 4 hr. at -10° to -15° and for 8 hr. at 0° to -3°. The mixture then was hydrolyzed with 30 ml. of saturated ammonium chloride solution, and the separated organic layer was dried over anhydrous calcium chloride. The dry organic layer was distilled rapidly at low pressure into a receiver cooled to -78°. Fractional distillation of the distillate gave 23 g. (42% yield) of triethylperfluorovinylsilane, b.p. 30° (8.8 mm.) to

36° (9.5 mm.). A second distillation gave 22 g. of pure material, b.p. 35° (9.6 mm.), $n^{25}D$ 1.4003.

<u>Anal.</u> Calcd. for $C_8H_{15}F_3Si$: C, 48.95; H, 7.70; F, 29.04.

Found: C, 49.19; H, 7.95; F, 29.08.

<u>Reaction of Triethylperfluorovinylsilane with Organolithium Reagents.</u> -

The reaction with phenyllithium is described as an example of the procedure used.

To 40 ml. of 1.14M solution of phenyllithium in ether under an atmosphere of nitrogen was added 8.0 g. (0.04 mole) of triethylperfluorovinylsilane. A white solid precipitated. The reaction mixture was stirred for 3 hr. at room temperature, cooled to 0°, carefully hydrolyzed with saturated ammonium chloride solution, and filtered. Distillation of the dried organic layer gave a colorless fraction boiling 90-96° (0.75 mm.) and 1.0 g. of a viscous, yellow residue. A second fractional distillation resulted in 0.2 g. of liquid of b.p. 72-81° (0.3 mm.), $n^{25}D$ 1.5091, and 7.9 g. (76%) of $Et_3SiCF=CFC_6H_5$, b.p. 81-84° (0.25 mm.), $n^{25}D$ 1.5117 to 1.5113. Another distillation gave the pure compound, b.p. 91° (0.55 mm.), $n^{25}D$ 1.5112.

<u>Anal.</u> Calcd. for $C_{14}H_{20}F_2Si$: C, 66.09; H, 7.92; F, 14.93.

Found: C, 66.37; H, 7.92; F, 14.65.

The reaction of vinyllithium[22] with triethylperfluorovinylsilane gave

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(22) D. Seyferth and M. A. Weiner, <u>Chemistry and Industry (London)</u>, 402 (1959); <u>J. Am. Chem. Soc.</u>, <u>83</u>, 0000 (1961).

$Et_3SiCF=CFCH=CH_2$ in 48% yield, b.p. 44.5° (1.1 mm.), $n^{25}D$ 1.4556.

<u>Anal</u>. Calcd. for $C_{10}H_{18}F_2Si$: C, 58.79; H, 8.88; F, 18.59.

Found: C, 58.88; H, 8.70· F, 18.58.

A similar reaction with allyllithium[23] gave $Et_3SiCF=CFCH_2CH=CH_2$, (55%), b.p. 51° (1.6 mm.), $n^{25}D$ 1.4382.

<u>Anal</u>. Calcd. for $C_{11}H_{20}F_2Si$: C, 60.50; H, 9.32; F, 17.40.

Found: C, 60.34; H, 9.33; F, 17.48.

$Et_3SiCF=CFC_4H_9$, b.p. 53° (0.4 mm.), $n^{25}D$ 1.4309, was obtained in 79% yield by the action of n-butyllithium on triethylperfluorovinylsilane.

<u>Anal</u>. Calcd. for $C_{12}H_{24}F_2Si$: C, 61.49; H, 10.32; F, 16.21.

Found: C, 61.72; H, 10.72; F, 15.96.

<u>Reaction of Triethylperfluorovinylsilane with Triphenylsilyllithium and Triphenylgermyllithium</u>. - A solution of triphenylsilyllithium[24] was prepared

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(23) D. Seyferth and M. A. Weiner, <u>J. Org. Chem.</u>, <u>24</u>, 1395 (1959).

(24) H. Gilman and G. D. Lichtenwalter, <u>J. Am. Chem. Soc.</u>, <u>80</u>, 608 (1958).

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by cleavage of 10 g. (0.02 mole) of hexaphenyldisilane with 2 g. (0.29 g. atom) of finely cut lithium wire in 70 ml. THF. To 5.9 g. (0.03 mole) of triethylperfluorovinylsilane in a small volume of THF at 0° under nitrogen was added dropwise with stirring 50 ml. of the triphenylsilyllithium solution. The resulting mixture was stirred for one hr. at room temperature. During this time the color of the lithium reagent was discharged, and a white precipitate formed. The reaction mixture was left at room temperature overnight, hydrolyzed with saturated ammonium chloride solution and filtered. The dried organic layer was evaporated. The residue crystallized on cooling

to 0° for some time to give 9.5 g. of white crystalline solid. This solid dissolved in part in pentane; the insoluble portion was filtered. Evaporation of the pentane solution left 9.0 g. of white platelets, m.p. 70-73°, a yield of 67%. Recrystallization from methylene chloride gave pure $Et_3SiCF=CFSi(C_6H_5)_3$, m.p. 73.6-75°.

Anal. Calcd. for $C_{26}H_{30}F_2Si_2$: C, 71.51; H, 6.92; F, 8.70.

Found: C, 71.68; H, 6.92; F, 8.62.

A similar procedure was followed in the reaction of triphenylgermyl-lithium[25] with triethylperfluorovinylsilane in ethylene glycol dimethyl ether.

(25) H. Gilman and C. W. Gerow, J. Am. Chem. Soc., 77, 5509 (1955).

The product, $Et_3SiCF=CFGe(C_6H_5)_3$, m.p. 64-66°, was obtained in 55% yield.

Anal. Calcd. for $C_{26}H_{30}F_2SiGe$: C, 66.27; H, 6.42; F, 8.06.

Found: C, 66.01; H, 6.23; F, 7.83.

Reaction of Triethylperfluorovinylsilane with Diphenylphosphinyllithium. -

To 1.0 g. (0.14 g. atom) of lithium suspended in 20 ml. THF was added a solution of 8.0 g. of diphenylbromophosphine in 30 ml. THF. The reaction mixture was stirred and maintained at -25°. The initially pale yellow solution changed to bright red as the reaction proceeded. The reagent solution was stirred at -25° for 3 hr. To 5.9 g. (0.03 mole) of triethylperfluoro-vinylsilane in 20 ml. THF at 0° was added dropwise the $(C_6H_5)_2PLi$ solution. The bright red color of the latter changed to dark brown. The reaction mixture was stirred at 0° for 2 hr. and then left to stand overnight at this temperature. Upon removal of solvent a dark brown, viscous liquid remained.

Distillation gave 7.0 g. of colorless liquid, boiling range 70-162° (0.2

mm.). Fractional distillation of the latter resulted in 1.3 g., boiling

range 57-153° (0.35 mm.) and 5.8 g. (53%) of colorless liquid, b.p. 153-

155° (0.35 mm.), $n^{25}D$ 1.5619. This was identified to be $Et_3SiCF=CFP(C_6H_5)_2$.

Anal. Calcd. for $C_{20}H_{25}F_2PSi$: C, 66.27; H, 6.95; F, 10.48; P, 8.55.

Found: C, 66.38; H, 7.18; F, 10.60; P, 8.62.

Attempted quaternization of this product with methyl iodide resulted

in partial cleavage of the $Et_3SiCF=CF-$ group. To 1.8 g. (5 mmoles) of

$Et_3SiCF=CFP(C_6H_5)_2$ in 20 ml. of ether was added 1.5 g. (11 mmoles) of methyl

iodide. The mixture was refluxed for 30 min. Removal of volatiles left a

viscous liquid which crystallized partially after several weeks. Recrystal-

lization of the solid which had formed from acetone gave 0.6 g. (35%) of

dimethyldiphenylphosphonium iodide, m.p. 240° (dec.).

Anal. Calcd. for $C_{14}H_{16}PI$: C, 49.14; H, 4.71; P, 9.05; I, 37.09.

Found: C, 49.42; H, 5.09; P, 9.02; I, 37.13.

Reaction of Triethylperfluorovinylsilane with Phenylmagnesium Bromide. -

The Grignard reagent was prepared from 5.5 g. (0.23 g. atom) of magnesium

turnings and 31.5 g. (0.2 mole) of bromobenzene in 100 ml. THF. To 5.9 g.

(0.03 mole) of triethylperfluorovinylsilane was added 20 ml. of the phenyl

Grignard solution, and the resulting mixture was stirred at reflux for 24

hr. Hydrolysis with saturated ammonium chloride solution was followed by

filtration and distillation of the organic layer. The product, $Et_3SiCF=CFC_6H_5$,

b.p. 81-82° (0.2 mm.), $n^{25}D$ 1.5096, was isolated in 64% yield. The infrared

spectrum of the product was identical with that of $Et_3SiCF=CFC_6H_5$ prepared

via the phenyllithium-triethylperfluorovinylsilane reaction.

Anal. Calcd. for $C_{14}H_{20}F_2Si$: C, 66.09; H, 7.92; F, 14.93.

Found: C, 66.39; H, 8.16; F, 14.70.

Reaction of α,β-Difluoro-β-triethylsilylstyrene with Phenyllithium. -

(a) 1:1 Molar Ratio. - To 7.6 g. (0.03 mole) of $Et_3SiCF=CFC_6H_5$ in 80 ml.

1:1 ether-THF was added 35.3 ml. of 0.85M phenyllithium (0.03 mole) in ether.

The resulting mixture was refluxed for 4 hr., cooled to 0° and hydrolyzed

with saturated ammonium chloride solution until a neutral aqueous phase re-

sulted. The organic layer was dried, and subsequently the solvent was dis-

tilled off. The residue was separated into two fractions by distillation:

(1) 56-90° (0.25 - 0.3 mm.), 7.3 g., and (2) 90-110° (0.3 mm.), 1.4 g.

Fraction (1) was analyzed using gas chromatography (Dow Corning 710 Silicone

Fluid on firebrick; helium carrier gas at 14 p.s.i.; preheater at 300° and

jacket at 220°). It was found to consist of 41% triethylphenylsilane, 2%

biphenyl, 37% $Et_3SiCF=CFC_6H_5$ and 19% diphenylacetylene (elution in that

order). Triethylphenylsilane was isolated in macro amounts by preparative

scale gas chromatography, $n^{25}D$ 1.5006 (lit.[26] $n^{25.1}D$ 1.5004). Its infrared

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(26) A. Bygdén, Z. physikal. Chem., 90, 243 (1915).

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spectrum was identical with that of an authentic sample prepared by the

reaction of triethylchlorosilane with phenyllithium in ether. α,β-Difluoro-

β-triethylsilylstyrene was identified by its infrared spectrum and its

refractive index ($n^{25}D$ 1.5112). Fraction (2) solidified on standing at

room temperature. It was dissolved in a minimum amount of xylene and analyzed

by gas chromatography: 1% triethylphenylsilane, 27% $Et_3SiCF=CFC_6H_5$ and

72% diphenylacetylene. The latter was identified by isolation (m.p.

60-60.5°). No depression of m.p. occurred when the substance was mixed

with authentic diphenylacetylene, and the infrared spectra of the product

and of authentic diphenylacetylene were superimposable.

Anal. Calcd. for $C_{14}H_{10}$: C, 94.50; H, 5.63. Found: C, 94.50; H, 5.48.

The gas chromatography data allowed the following approximate yields to

be calculated (based on starting silane): triethylphenylsilane, 50%;

starting silane, 41% recovery; diphenylacetylene, 45%.

(b) 1:2 Molar Ratio. - The same procedure was used in the reaction of 10.2

g. (0.04 mole) of $Et_3SiCF=CFC_6H_5$ in 60 ml. THF with 80 ml. of 1.1M phenyl-

lithium (0.088 mole) in ether. The residue remaining after removal of sol-

vent was separated into three fractions by distillation: (1) 54-59° (0.2-

0.35 mm.), 7.4 g.; (2) 65-75° (0.3-0.25 mm.), 0.6 g.; (3) 90-100° (0.25-

0.35 mm.), 3.5 g. Each fraction was analyzed by gas chromatography. Frac-

tion (1): 96% triethylphenylsilane, 4% biphenyl; fraction (2): 71% tri-

ethylphenylsilane, 17% biphenyl, 12% diphenylacetylene; fraction (3) (as

a 50% xylene solution): 6% triethylphenylsilane, 4% biphenyl, 90% diphenyl-

acetylene. In addition, 2.1 g. of diphenylacetylene was isolated from the

distillation apparatus after these fractions had been taken. These data

gave the following yields: triethylphenylsilane, 97%; diphenylacetylene,

71% (based on starting silane). The distillation residue consisted of the

diphenylacetylene mentioned above and black, apparently polymeric solid.

Reaction of Triethylperfluorovinylsilane with Sodium Ethoxide. -

(a) In Ethanol Solution. - Sodium (0.5 g., 0.022 g. atom) was dissolved in

5 g. of anhydrous ethanol. The resulting solution was cooled to 0° and 5.9 g. (0.03 mole) of triethylperfluorovinylsilane was added. The mixture was stirred and allowed to warm to room temperature. A vigorous reaction commenced and continued for a few minutes. After the mixture had been stirred for 16 hr. at room temperature, it was diluted with 50 ml. of pentane. Dry carbon dioxide was bubbled in to precipitate sodium carbonate. The mixture was filtered and the filtrate fractionally distilled. Triethylethoxysilane, b.p. 30° (3.8 mm.) to 32° (4.0 mm.), $n^{25}D$ 1.4111, was obtained in 69% yield (2.9 g.). Another distillation gave pure material. Anal. Calcd. for $C_8H_{20}OSi$: C, 59.92; H, 12.57. Found: C, 59.94; H. 12.79. A higher fraction, b.p. 47.5-49° (0.9-1.1 mm.); redistilled, b.p. 36.5° (0.4 mm.), $n^{25}D$ 1.4252; was identified at $Et_3SiCF=CFOC_2H_5$. This product was isolated in 28% yield (1.8 g.).

Anal. Calcd. for $C_{10}H_{20}OF_2Si$: C, 54.02; H, 9.07; F, 17.09.

Found: C, 54.49; H, 9.59; F, 17.10.

(b) In Tetrahydrofuran Solution. - A suspension of 0.03 mole of dry sodium ethoxide in 19 ml. THF was added to 5.9 g. (0.03 mole) of triethylperfluoro-vinylsilane in 20 ml. THF at 0°. The mixture was stirred at room temperature for 2 hr. and subsequently quenched by bubbling in dry gaseous carbon dioxide. The precipitate was filtered and the filtrate distilled to give 2.3 g. of triethylethoxysilane (48%), b.p. 39° (8 mm.), and 2.6 g. of $Et_3SiCF=CFOEt$ (39%), b.p. 48.5° (0.95 mm.), $n^{25}D$ 1.4252.

Anal. Found: C, 54.05; H, 9.37.

Reaction of Triethylperfluorovinylsilane with Sodium Trimethylsilylmethoxide. - Sodium trimethylsilylmethoxide was prepared by dissolving 0.7 g. (0.03 g.

atom) of sodium in a mixture of 3.2 g. (0.03 mole) of trimethylsilylmethanol[27]

(27) Prepared according to D. Seyferth, J. Am. Chem. Soc., 81, 1844 (1959).

and 20 ml. diethyl ether. To the resulting turbid solution was added 5.9 g.

of triethylperfluorovinylsilane in 15 ml. of ether at a rate sufficient to

maintain a gentle reflux. The solution was stirred for 3 hr. at room tem-

perature and left to stand overnight. Filtration was followed by fractional

distillation to give 1.7 g. of colorless liquid, b.p. 48-51° (1.9 mm.), n^{25}_D

1.4238, and 5.6g.(66%) of $Et_3SiCF=CFOCH_2SiMe_3$, b.p. 70° (0.65 mm.), n^{25}_D

1.4362.

<u>Anal</u>. Calcd. for $C_{12}H_{26}OF_2Si_2$: C, 51.38; H, 9.34; F, 13.55.

Found: C, 51.55; H, 9.62; F, 13.47.

The lower boiling fraction is believed to be an azeotropic mixture of

$Et_3SiOCH_2SiMe_3$ and $Et_3SiCF=CFOCH_2SiMe_3$, since its infrared spectrum showed

strong absorption in the C=C region.

<u>Reaction of Triethylperfluorovinylsilane with Sodium n-Propylmercaptide</u>

<u>and Sodium Thiophenolate.</u> - To 3.0 g. (0.03 mole) of sodium n-propylmercap-

tide (prepared by dissolving sodium in the calculated amount of n-propyl-

mercaptan) suspended in 20 ml. THF was added 5.9 g. of triethylperfluoro-

vinylsilane. The resulting mixture was heated at reflux for 18 hr. under

nitrogen. Pentane (25 ml.) was added, and the mixture was filtered. The

filtrate was distilled to give 1.3 g. (22% recovery) of triethylperfluoro-

vinylsilane, b.p. 36.5-37.5° (11-13 mm.), and 4.5 g. (76% yield based on

unrecovered silane) of $Et_3SiCF=CFSC_3H_7$, b.p. 65° (0.35 mm.), n^{25}_D 1.4640.

Anal. Calcd. for $C_{11}H_{22}F_2SSi$: C, 52.34; H, 8.79; F, 15.06; S, 12.68.

Found: C, 52.54; H, 8.91; F, 14.99; S, 12.30.

A similar reaction carried out on the same scale with sodium thiophenolate in THF suspension resulted in isolation of 7.5 g. (87%) of $Et_3SiCF=CFSC_6H_5$, b.p. 101.5° (0.3 mm.), $n^{25}D$ 1.5217.

Anal. Calcd. for $C_{14}H_{20}F_2SSi$: C, 58.70; H, 7.04; F, 13.27; S, 11.19.

Found: C, 58.83; H, 7.23; F, 12.98; S, 11.11.

Nuclear Resonance Spectra. - F^{19} Nuclear resonance spectra were measured by Mr. L. F. Herrick at Harvard University using a Varian V-4300B NMR Spectrometer equipped with a superstabilizer, sample spinner and a Sanborn 151 Recorder, and operating at 56.4 Mc. The solid compounds, $Et_3SiCF=CFM(C_6H_5)_3$ (M= Si and Ge), were measured as a solution in benzene; in all other cases pure liquid samples were used which contained CCl_3F used as the internal reference. Chemical shifts are reported to be accurate to 1%. The lines observed are reported in p.p.m. relative to the CCl_3F standard.

$Et_3SiCF=CFC_6H_5$: 152.4, 154.6, 163.8, 166.0 p.p.m.; J_{FF} 124 c.p.s.

$Et_3SiCF=CFC_4H_9$: 145.7, 147.9 (with secondary splitting of 23 c.p.s.),
172.9, 175.1 p.p.m. (with secondary splitting of 5.8 c.p.s.);
J_{FF} 126 c.p.s.

$Et_3SiCF=CFCH_2CH=CH_2$: 141.7, 143.9 (with secondary splitting of 23 c.p.s.),
168.4, 170.6 p.p.m. (with secondary splitting of 6 c.p.s.);
J_{FF} 126 c.p.s.

$Et_3SiCF=CFSi(C_6H_5)_3$: 152.7, 155.0, 159.1, 161.5 p.p.m.; J_{FF} 132 c.p.s.

$Et_3SiCF=CFGe(C_6H_5)_3$: 153.2, 155.7, 157.2, 159.7 p.p.m.; J_{FF} 144 c.p.s.

$Et_3SiCF=CFSC_3H_7$: 128.2, 130.8, 148.1, 150.6 p.p.m.; J_{FF} 147 c.p.s.

$Et_3SiCF=CFSC_6H_5$: 96, 96.5, 120, 120.5, p.p.m. J_{FF} (cis) 20 c.p.s. ;

126.0, 128.6, 143.0, 145.6 p.p.m.; J_{FF} (trans)

148 c.p.s.

$Et_3SiCF=CFOC_2H_5$: 117.1, 119.3, 193.0, 195.2, p.p.m. J_{FF} 122 c.p.s.

$Et_3SiCF=CFOCH_2SiMe_3$: 118.3, 120.4, 192.1, 194.3 p.p.m.; J_{FF} 122 c.p.s.